

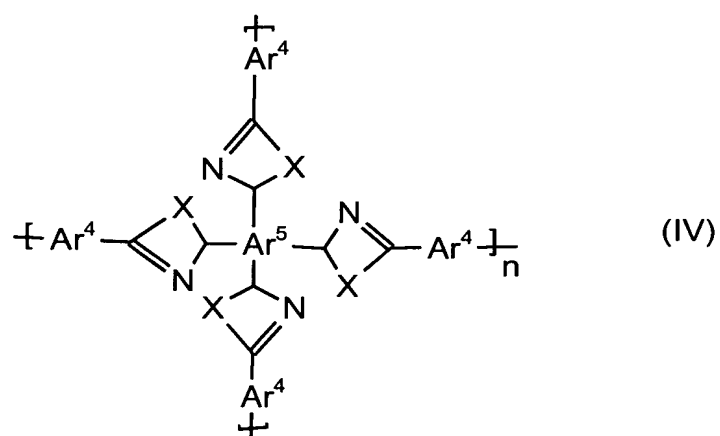
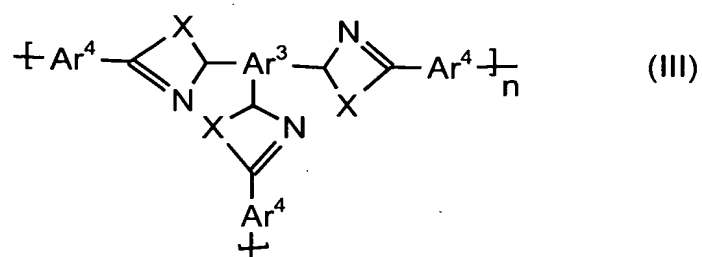
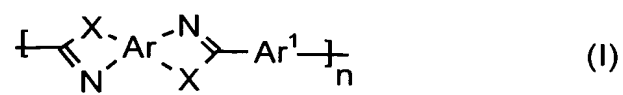
What is claimed is:

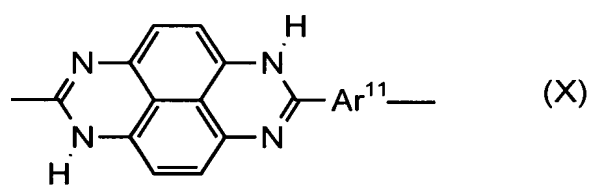
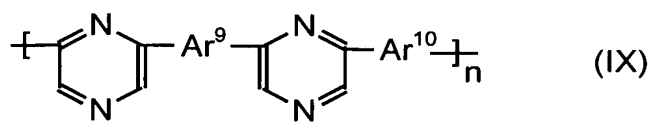
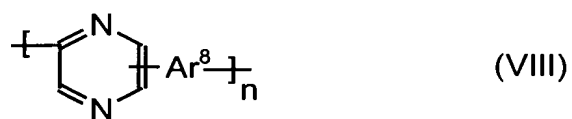
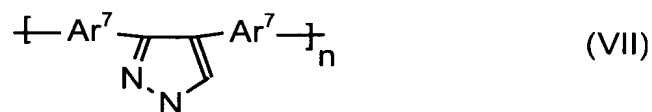
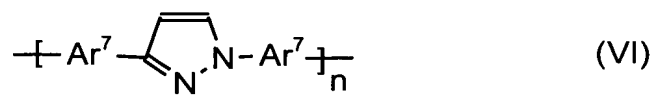
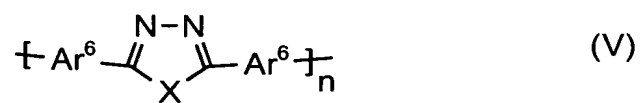
1. A proton-conducting polymer membrane based on polyazoles, obtainable by a process comprising the steps of
 - 5 A) mixing one or more aromatic tetraamino compounds having a high phosphoric acid affinity or low phosphoric acid affinity with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer which have a high phosphoric acid affinity or low phosphoric acid affinity,
10 or mixing one or more aromatic and/or heteroaromatic diaminocarboxylic acids having a high phosphoric acid affinity in polyphosphoric acid to form a solution and/or dispersion
 - B) heating the mixture from step A), preferably under inert gas, and polymerizing until an intrinsic viscosity of up to 1.5 dl/g, preferably from 0.3 to 1.0 dl/g, in
15 particular from 0.5 to 0.8 dl/g, is obtained to form a polymer whose phosphoric acid affinity is greater than the phosphoric acid affinity of the polymer formed in step D),
 - C) mixing one or more aromatic tetraamino compounds having a high phosphoric acid affinity or low phosphoric acid affinity
20 with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer which have a high phosphoric acid affinity or low phosphoric acid affinity, in polyphosphoric acid to form a solution and/or dispersion
 - D) heating the mixture from step C), preferably under inert gas, and polymerizing
25 until an intrinsic viscosity of up to 1.5 dl/g, preferably from 0.3 to 1.0 dl/g, in particular from 0.5 to 0.8 dl/g, is obtained to form a polymer whose phosphoric acid affinity is less than the phosphoric acid affinity of the polymer formed in step B),
 - E) combining the polymer from step B) and the polymer from step D), the phosphoric acid affinity of the polymer from step B) being greater than the phosphoric acid affinity of the polymer from step D),
 - 30 F) applying a layer using the mixture according to step E) on a carrier or on an electrode,
 - G) heating the sheetlike structure/layer obtainable according to step F),
35 preferably under inert gas, until an intrinsic viscosity of more than 1.5 dl/g, preferably of more than 1.8 dl/g, in particular of more than 1.9 dl/g, is attained to form a polyazole block polymer,
 - H) treating the membrane formed in step G) (until it is self-supporting).

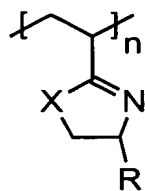
2. The membrane as claimed in claim 1, characterized in that the aromatic tetraamino compounds having a high phosphoric acid affinity used are 2,3,5,6-tetraaminopyridine, 3,3',4,4'-tetraaminodiphenylsulfone, 3,3',4,4'-tetraaminodiphenyl ether and salts thereof, especially the mono-, di-, tri- and tetrahydrochloride derivatives thereof.
3. The membrane as claimed in claim 1, characterized in that the aromatic tetraamino compounds having a low phosphoric acid affinity used are 3,3',4,4'-tetraaminobiphenyl, 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane and salts thereof, especially the mono-, di-, tri- and tetrahydrochloride derivatives thereof.
4. The membrane as claimed in claim 1, characterized in that the aromatic carboxylic acids having a high phosphoric acid affinity used are pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,6-dihydroxyisophthalic acid, 4,6-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid and diphenylsulfone-4,4'-dicarboxylic acid.
5. The membrane as claimed in claim 1, characterized in that the aromatic carboxylic acids having a low phosphoric acid affinity used are isophthalic acid, terephthalic acid, phthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, diphenyl ether 4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid and 4-carboxycinnamic acid.

6. The membrane as claimed in claim 1, characterized in that the diaminocarboxylic acids having a high phosphoric acid affinity used are diaminobenzoic acid and the mono and dihydrochloride derivatives thereof, and also 1,2-diamino-3'-carboxy acid 4,4'-diphenyl ether.
7. The membrane as claimed in claim 1, characterized in that the aromatic carboxylic acids used are tricarboxylic acids, tetracarboxylic acids or the C1-C20-alkyl esters or C5-C12-aryl esters thereof or the acid anhydrides thereof or the acid chlorides thereof, preferably 1,3,5-benzenetricarboxylic acid (trimesic acid); 1,2,4-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid and/or 2,4,6-pyridinetricarboxylic acid.
8. The membrane as claimed in claim 1, characterized in that the aromatic carboxylic acids used are tetracarboxylic acids, the C1-C20-alkyl esters or C5-C12-aryl esters thereof or the acid anhydrides thereof or the acid chlorides thereof, preferably benzene-1,2,4,5-tetracarboxylic acids; naphthalene-1,4,5,8-tetracarboxylic acids, 3,5,3',5'-biphenyltetracarboxylic acid; benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid.
9. The membrane as claimed in claim 4, characterized in that the content of tricarboxylic acid or tetracarboxylic acids (based on dicarboxylic acid used) is between 0 and 30 mol%, preferably 0.1 and 20 mol%, in particular 0.5 and 10 mol%.
10. The membrane as claimed in claim 1, characterized in that the heteroaromatic carboxylic acids used are heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids which contain at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatic, preferably pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and also the C1-C20-alkyl esters or C5-C12-aryl esters thereof, or the acid anhydrides thereof or the acid chlorides thereof.

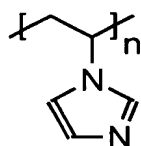
11. The membrane as claimed in claim 1, characterized in that a polyphosphoric acid having a content, calculated as P_2O_5 (by acidimetry), of at least 83% is obtained in step A) and C).
- 5 12. The membrane as claimed in claim 1, characterized in that a solution or a dispersion/suspension is obtained in step A) and C).
- 10 13. The membrane as claimed in claim 1, characterized in that block polymers based on polyazole and comprising repeat azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)



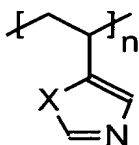




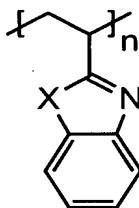
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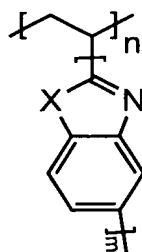
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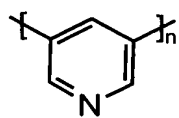
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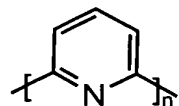
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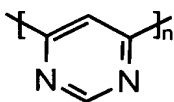
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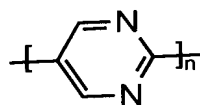
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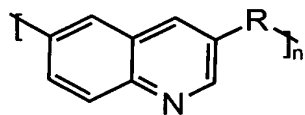
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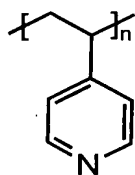
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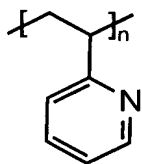
(XIX)



(XX)



(XXI)



(XXII)

in which

Ar are the same or different and are each a tetravalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar¹ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar² are the same or different and are each a di- or trivalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar³ are the same or different and are each a trivalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar⁴ are the same or different and are each a trivalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar⁵ are the same or different and are each a tetravalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar⁶ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar⁷ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar⁸ are the same or different and are each a trivalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar⁹ are the same or different and are each a di- or tri- or tetravalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar¹⁰ are the same or different and are each a di- or trivalent aromatic or heteroaromatic group which may be mono- or polycyclic,

Ar¹¹ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mono- or polycyclic,

X are the same or different and are each oxygen, sulfur or an amino group which bears a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical,

R is the same or different and is hydrogen, an alkyl group or an aromatic group, with the proviso that R in formula (XX) is not hydrogen, and

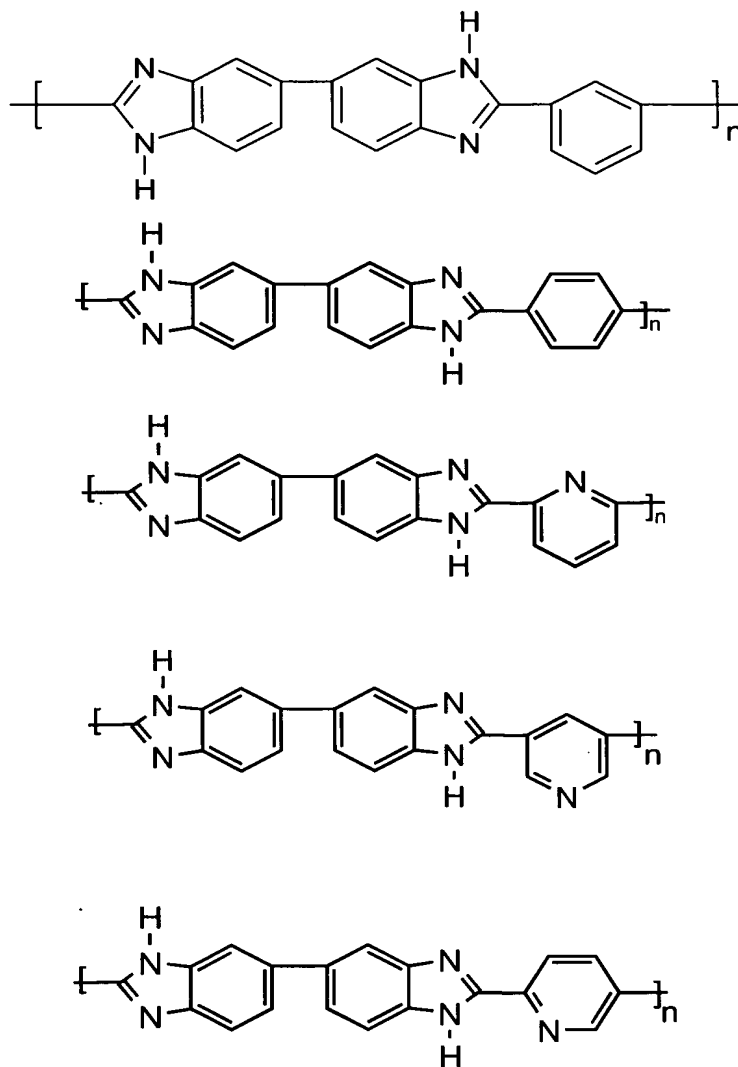
n, m are each an integer greater than or equal to 10, preferably greater than or equal to 100,

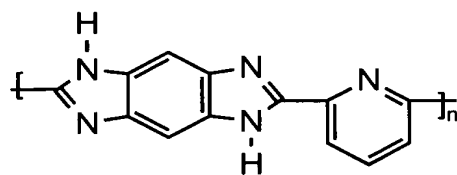
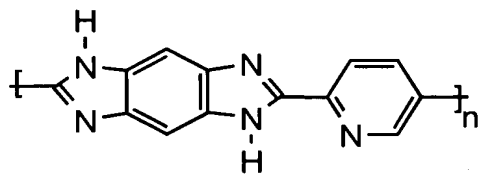
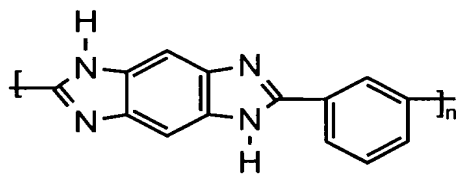
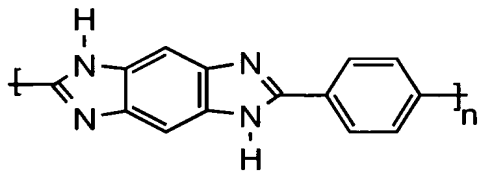
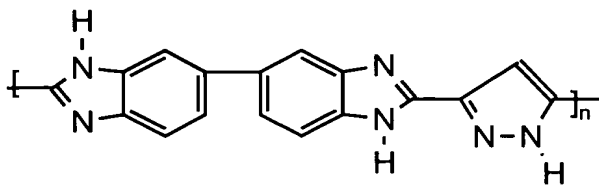
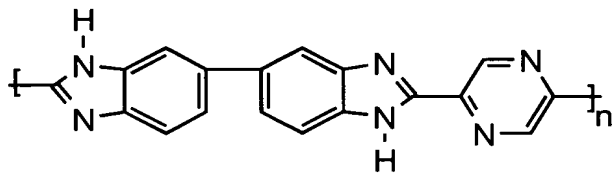
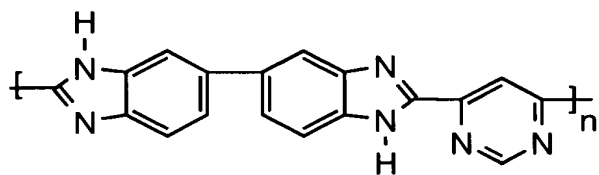
are formed in step G).

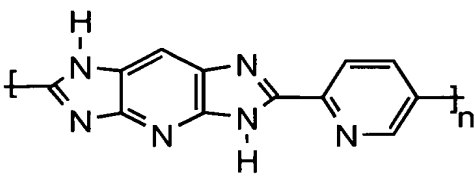
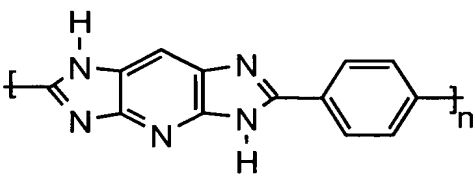
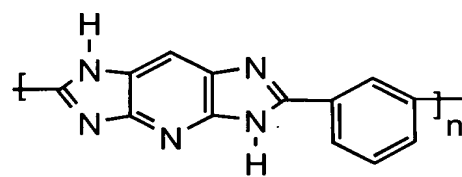
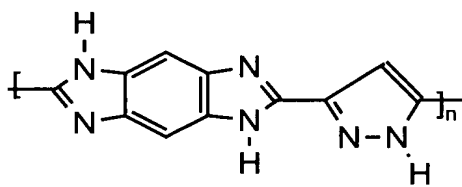
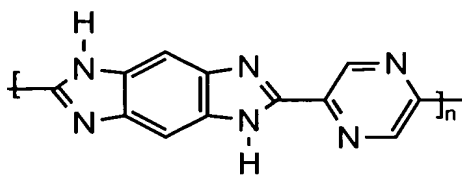
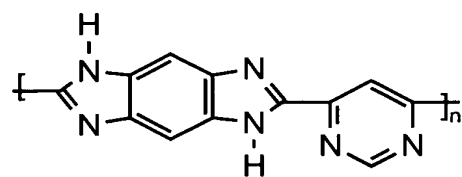
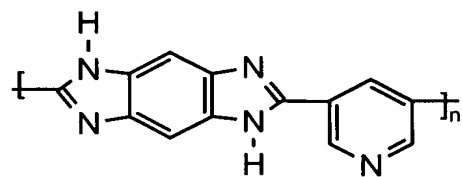
14. The membrane as claimed in claim 1, characterized in that a block polymer containing repeat segments selected from the group of polybenzimidazole, poly(pyridines), poly(pyrimidines), polyimidazoles, polybenzothiazoles,

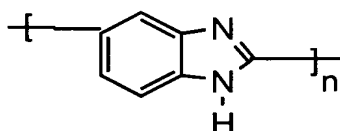
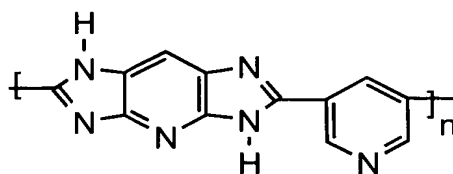
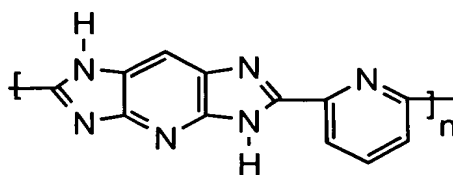
polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles and poly(tetraazapyrenes) is formed in step G).

15. The membrane as claimed in claim 1, characterized in that a block polymer containing repeat benzimidazole units of the formula

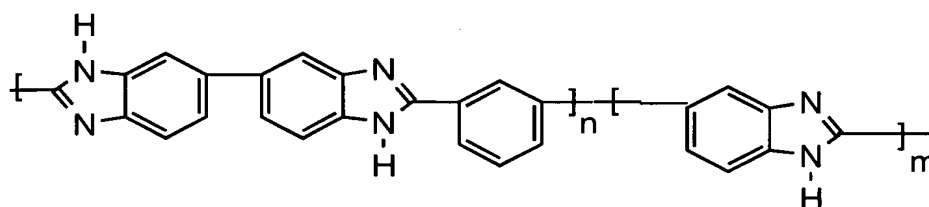
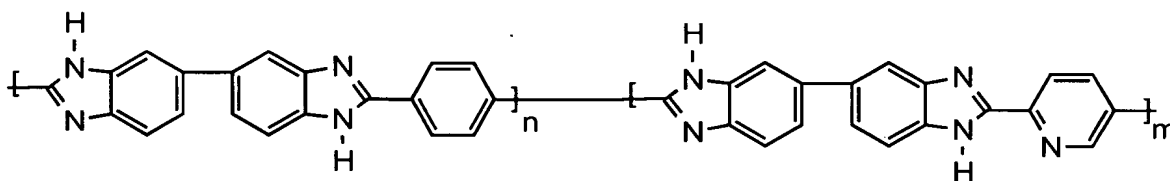








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where n and m are each an integer greater than or equal to 10, preferably greater than or equal to 100, is formed in step G).

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16. The membrane as claimed in claim 1, characterized in that the membrane obtained in step H) is treated in the presence of moisture at temperatures and for a period until the membrane is self-supporting and can be removed from the carrier without damage.

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17. The membrane as claimed in claim 1, characterized in that the membrane is treated in step H) at temperatures above 0°C and 150°C, preferably at

temperatures between 10°C and 120°C, in particular between room temperature (20°C) and 90°C, in the presence of moisture or water and/or steam.

- 5 18. The membrane as claimed in claim 1, characterized in that the treatment of the membrane in step H) is between 10 seconds and 300 hours, preferably from 1 minute to 200 hours.
- 10 19. The membrane as claimed in claim 1, characterized in that the carrier selected in step F) is an electrode and the treatment in step H) is such that the membrane formed is no longer self-supporting.
- 15 20. The membrane as claimed in claim 1, characterized in that a layer having a thickness of 20 and 4000 μm , preferably between 30 and 3500 μm , in particular between 50 and 3000 μm is obtained in step F).
- 20 21. The membrane as claimed in claim 1, characterized in that the membrane formed by step H) has a thickness between 15 and 3000 μm , preferably between 20 and 2000 μm , in particular between 20 and 1500 μm .
- 25 22. An electrode which having a proton-conducting polymer coating based on polyazoles, obtainable by a process comprising the steps of
 - A) mixing one or more aromatic tetraamino compounds having a high phosphoric acid affinity or low phosphoric acid affinity

with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer which have a high phosphoric acid affinity or low phosphoric acid affinity,

or mixing one or more aromatic and/or heteroaromatic diaminocarboxylic acids having a high phosphoric acid affinity in polyphosphoric acid to form a solution and/or dispersion

30
 - B) heating the mixture from step A), preferably under inert gas, and polymerizing until an intrinsic viscosity of up to 1.5 dl/g, preferably from 0.3 to 1.0 dl/g, in particular from 0.5 to 0.8 dl/g, is obtained to form a polymer whose phosphoric acid affinity is greater than the phosphoric acid affinity of the polymer formed in step D),

35
 - C) mixing one or more aromatic tetraamino compounds having a high phosphoric acid affinity or low phosphoric acid affinity

with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer which have a high

phosphoric acid affinity or low phosphoric acid affinity, in polyphosphoric acid to form a solution and/or dispersion

- 5 D) heating the mixture from step C), preferably under inert gas, and polymerizing until an intrinsic viscosity of up to 1.5 dl/g, preferably from 0.3 to 1.0 dl/g, in particular from 0.5 to 0.8 dl/g, is obtained to form a polymer whose phosphoric acid affinity is less than the phosphoric acid affinity of the polymer formed in step B),
- 10 E) combining the polymer from step B) and the polymer from step D), the phosphoric acid affinity of the polymer from step B) being greater than the phosphoric acid affinity of the polymer from step D),
- F) applying a layer using the mixture according to step E) on an electrode,
- 15 G) heating the sheetlike structure/layer obtainable according to step F), preferably under inert gas, until an intrinsic viscosity of more than 1.5 dl/g, preferably of more than 1.8 dl/g, in particular of more than 2.0 dl/g, is attained to form a polyazole block polymer,
- H) treating the membrane formed in step G).
- 20 23. The electrode as claimed in claim 22, the coating having a thickness between 2 and 3000 μm , preferably between 3 and 2000 μm , in particular between 5 and 1500 μm .
24. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in one or more of claims 1 to 21.
- 25 25. A membrane-electrode unit comprising at least one electrode as claimed in claim 22 or 23 and at least one membrane as claimed in one or more of claims 1 to 21.
- 30 26. A fuel cell comprising one or more membrane-electrode units as claimed in claim 24 or 25.